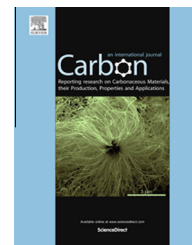


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Competition between carboxylic and phenolic groups for the preferred sites at the periphery of graphene – A DFT study

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ABSTRACT

The energetics of placing carboxyl and phenolic groups at the periphery of a graphene sheet are studied using density functional theory (B3LYP) with a 6-31G* basis set, augmented with diffuse functions on oxygen atoms. Individually both COOH and OH have the same preference for the corner sites, but in presence of COOH the smaller OH group opts for its second preference, the zigzag sites, leaving corner sites to the larger group. H-bonding acts to keep the two groups adjacent to one another, suggesting an interaction energy between the two groups of about 7.0 kcal/mol. However, π -conjugation between these groups with the carbon network plays a decisive role in the stability as well. Vibrational analyses reveal strong features that are characteristic of each site, which may help in the assignment of experimental spectra.

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1. Introduction

Graphene, discovered by a surprisingly simple technique [1], is the most recent addition to the multi-dimensional carbon nanomaterials family. The rapid advancement in graphene research is due to their unique properties [2–5]. Graphene (Gr) can be readily oxidized and the resulting properties strongly depend on the structures and on the number and positions of oxygen-containing groups. Research on the chemistry of such newly developed nanomaterials has just begun [6–8] and their characterization has become increasingly important, as small deviations from the method of preparation including starting materials lead to significant differences in structure and consequently in their properties.

Graphene oxide (GO), created during various oxidation processes, contains several oxygen containing groups, such as –COOH, –OH, ether, epoxy etc., at both edges and surface.

Due to strong dependence on the starting materials, oxidation processes, and degree of oxidation, the determination of structures of GO become very complicated. Several structural models of GO, such as that of Hofmann, Ruess, Scholz-Boehm and Nakajima-Matsuo (detail in Ref. [9]), have been proposed at an earlier phase of GO research. Based on later results of analytical techniques, those models were found inadequate to correctly describe structures of GO. As research progressed, several new models, such as Lerf et al. [10] and Szabó et al. [9], were proposed. Recently Szabó et al. [9], Dreyer et al. [11] and Zhu et al. [12] have critically analyzed different proposed GO models in review articles. However, recent findings suggested some new features, such as possibility of five- or six-membered lactols [13] and aggregation of oxygen atoms at the edges [14] of GO structures which were not envisioned earlier. In summary, structures of GO and also reduced GO (RGO) are still not fully understood

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and continuation of studies may reveal fruitful new information to define all of the structural details of these fascinating materials. Understanding of such structures will be essential to control and tune properties in developing application oriented products.

Rich chemistry of acid groups elevated the importance of GO/RGO as these groups can be used as anchors for further functionalization, and such chemical modification can create a wide range of derivatives to enrich graphene chemistry [15,16]. Knowledge about the location and distribution of these groups is still limited and a recent experimental study [17] indicated that carboxyl groups might exist mainly at the graphene edges. Recent theoretical study by our group [18] on the carboxylated graphene sheet, where only COOH groups were considered at different peripheral sites, revealed some new structural features. The energy and geometry of Gr-COOH is attributed to a competition between π -conjugation and steric repulsion factors. Out of three possible sites (corner, zigzag and armchair edges), -COOH groups prefer the corner sites due to the extension of π -conjugation of COOH with the aromatic ring, which maintains the planarity of the Gr-COOH. The second preferred site of COOH is the zigzag edge; occupation of the acid group at the armchair edge distorts the sheet significantly, which makes those sites least preferable.

However, GO/RGO contains several other oxygen containing groups and those may have significant influence on the structures and thus properties. Similar to COOH groups, phenolic OH groups are most likely present at the periphery of defect-free graphene sheet. In fact, a very recent experimental study by Liu et al. [19] revealed the dependence of the formation of different functional groups based on the amount of oxidant KMnO_4 . According to their study, oxidation first takes places at the edges or at the defect sites and produces -OH groups, and above a critical amount of oxidant OH groups convert to carboxylic groups. Thus, both groups are most likely present in GO/RGO depending on the amount of oxidant. Evidence of excited state proton transfer at different pH between COOH and OH groups, present at the ortho-position, has recently been reported by Konkena and Vasudevan [20,21]. These findings support the presence of both groups at the edges of Gr and if so, they are most likely connected by $\text{O}\cdots\text{H}-\text{O}$ hydrogen bonds.

Oxidized single-wall carbon nanotubes (SWNTs), where both COOH and OH groups are present at the tips, exhibit new structural features that have significant influence on the vibrational spectra [22], which was not envisioned earlier from fundamental concepts. For example, the estimated $\text{O}\cdots\text{H}-\text{O}$ hydrogen bond energy of 9–12 kcal/mol is almost double that found in simpler systems. Also, red-shifts of $\text{C}=\text{O}$ stretches and especially phenolic -OH stretching modes, involved in H-bonding, are amplified significantly in nanotubes. The magnitude of red or blue shift varies significantly depending on the interaction strengths and structural factors, such as chirality of tubes. Such changes in frequencies could be used to disentangle complicated IR spectra and identify locations of both groups. It is worth mentioning that our previous theoretical studies [23,24] revealed that the $\text{C}=\text{O}$ frequency of some COOH groups ($\sim 1650\text{ cm}^{-1}$) at the tip of

zigzag tubes is below the standard value ($\sim 1720\text{ cm}^{-1}$) a clear distinction from those tubes with their cousin armchair tubes.

Besides zigzag and armchair edges, corners of graphene are additional sites, where COOH groups have priority for the corner sites followed by the zigzag sites. Since experimental evidence supports the presence of OH group in addition to COOH, curiosity arises about their preference for different sites. Does the -OH group have the same preference as the COOH group? If so, then do they compete for the same site? What is the energy factor if they exchange positions? Do they prefer to stay closer to each other and form H-bond? If so, does their locations have any influence on such bonding, and if so, how much? What are the magnitudes of red-shift of participating modes in IR spectra when located on different sites of graphene? Resolving these issues would not only improve our understanding of the structure of GO/RGO, but may disclose some new principles, as noted in our previous studies [22,24,25], that are unusual and that might not fit into the current concept scheme of organic chemistry or H-bonding.

The present communication attempts to answer these questions. First we determine the preference of -OH groups and then consider both COOH and OH groups at a variety of different sites at the periphery of the graphene sheet. Multiple carboxyl and OH groups are added in order to examine how the presence of one group might affect the properties of another. The most stable isomers are identified, as are the energetic separations between various possible isomers. The effects of site selection upon the geometry of the functional groups, as well as the entire graphene sheet, are elucidated. Special emphasis is placed on calculating the IR spectra which offers the hope of allowing experimentalists to distinguish one sort of isomer from another.

Findings from this study may be generalized to many other extended conjugated systems, such as polycyclic aromatic hydrocarbon (PAH). Whatever their size and shape, all such systems may possess same sites (corner, zigzag and armchair) at their periphery as in graphene sheets. Thus, preference of acid and phenolic -OH groups, either alone or together, is expected to be similar for all cases.

2. Method of calculations

The B3LYP variant of density functional theory (DFT) [26,27] was used to include correlation effects. The accuracy of normal mode calculations using the B3LYP method is sufficiently good, and cost-to-benefit ratio optimal, with the 6-31G* basis set [28–31]. This split-valence double- ζ quality basis with five d-polarization functions was used for all carbon and hydrogen atoms. For proper description of electro-negative oxygen atoms, additional diffuse sp-functions were added to the 6-31G* basis; this combined basis set is denoted as 6-31G*(O+). This B3LYP/6-31G*(O+) method was earlier found reliable for predicting structures, energies and vibrational modes of oxidized SWNTs [23–25]. Geometries of chemically modified graphene sheets were fully optimized without any symmetry restriction, followed by vibrational analyses that insure the identification of true minima.

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